NEURAL NETWORK VS GUASSIAN PROCESS FITTING FOR REPRESENTING POTENTIAL ENERGY SURFACES

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Many methods have been proposed for fitting potential energy surfaces. Unfortunately, there are few comparative studies. In this paper, we compare neural networks (NN) with Gaussian process (GP) regression. We re-fit an accurate PES of formaldehyde and compare PES errors on the entire point set used to solve the vibrational Schrödinger equation, i.e. the only error that matters in quantum dynamics calculations. We also compare the vibrational spectra computed on the underlying reference PES and the NN and GP potential surfaces. The NN and GP surfaces are constructed with exactly the same points and the corresponding spectra are computed with the same points and the same basis. The GP fitting error is lower and the GP spectrum is more accurate. The best NN fits to 625/1250/2500 symmetry unique potential energy points have global PES root mean square errors (RMSE) of 6.53/2.54/0.86 cm-1, whereas the best GP surfaces have RMSE values of 3.87/1.13/0.62 cm-1, respectively. When fitting 625 symmetry unique points, the error the first 100 vibrational levels is only 0.06 cm-1 with the best GP fit, whereas the spectrum on the best NN PES has an error of 0.22 cm-1, with respect to the spectrum computed on the reference PES. This error is reduced to about 0.01 cm-1 when fitting 2,500 points with either NN or GP. We also find that the GP surface produces a relatively accurate spectrum when obtained based on as few as 313 points.